

Chemical versus van der Waals Interaction: The Role of the Heteroatom

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We performed first-principles calculations aimed to investigate the role of an heteroatom like N in the chemical and the long-range van der Waals (vdW) interactions for a flat adsorption of several π -conjugated molecules on the Cu(110) surface. Our study reveals that the alignment of the molecular orbitals at adsorbate-substrate interface depends on the number of heteroatoms. As a direct consequence, the molecule-surface vdW interactions involve not only π -like orbitals which are perpendicular to the molecular plane but also σ -like orbitals delocalized in the molecular plane.

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In the last decade, the molecular electronics emerged as a promising field able to provide the technology necessary to develop devices such as organic light-emitting diodes (OLEDs) [1, 2], organic field-effect transistors [3, 4, 5] or ultra-high-density memory circuits [6]. In this context, the ability to reliably describe the electronic properties [7, 8] or the mechanical manipulation process of molecules [9, 10] on surfaces is essential to understand and design the functionality of such devices. The achievement of these goals strongly depends on the accuracy of the state-of-the-art theoretical methods used to assess the interaction between a molecule or a molecular layer and a substrate of choice. Nowadays, the density functional theory (DFT) is the theoretical tool of choice to analyze [7, 8, 11, 12] and to predict [13, 14] the electronic properties of systems characterized by strong chemical bonds.

However, the loosely bounded physical systems [15] represent one of the major challenges for DFT because the effective Kohn-Sham (KS) potential does not exhibit the correct asymptotic behavior. In particular, the currently used exchange correlation energy functionals like the local density approximation (LDA) or the generalized gradient approximation (GGA) do not properly describe the long-range van der Waals (vdW) interactions. For instance, the GGA fails to predict a bonding ground-state for a van der Waals system like graphite [16].

One way to circumvent this limit is to include the dispersion effects in DFT in a semiempirical fashion, in which the total energy of the physical system is a sum of the self-consistent Kohn-Sham energy as obtained from the DFT calculations and semiempirical dispersion correction which depends on the interatomic distance. For example, a semiempirical treatment of the vdW dispersions in *ab initio* calculations was used to investigate, for instance, the adenine on graphite(0001) [17].

Another way to accurately account for the vdW interactions is a first-principle approach [18] which requires the calculation of a nonlocal correlation energy functional

as a post GGA perturbation procedure. This method was successfully employed to investigate the benzene, naphthalene and phenol on graphite(0001) [19] and α -Al₂O₃(0001) or thiophene on Cu(110) [20] surfaces.

In this Letter, we investigate the role of the heteroatoms on the chemical and the van der Waals interactions for a flat adsorption geometry on the Cu(110) surface of three prototype π -electron systems as benzene (Bz), pyridine (Py) and pyrazine (Pz) molecules. Our *ab initio* simulations reveal that, for the Bz the long-range dispersion effects are basically important only for the adsorption energy. This is not the case of the Py and Pz, where due to their low lying π -orbitals, the inclusion of the long-range correlations drastically influence the adsorption geometry and electronic structure, i. e. the Py becomes chemisorbed on the surface while the Pz binds to the surface mostly due to the van der Waals interaction. To evaluate the dispersion effects we used the *ab initio* (vdW-DF)[18] as well as a semiempirical (DFT-D) [21, 22] method. In particular, a key result of our study is that a state of the art investigation of the bonding mechanism leading to a flat molecule-substrate adsorption geometry requires the use of both methods to correctly describe the adsorption-geometry, the electronic structure and the correlation effects of the molecule-surface interface. Moreover, we show that the nature of the molecular orbitals involved in the dispersion interactions depends on the alignment of these orbitals with respect to the Fermi level of the adsorbate-surface system.

Our first-principles total-energy calculations are carried out in the framework of density functional theory (DFT) by employing the generalized gradient approximation (GGA) in a pseudopotential plane-wave formulation (projector augmented wave method) [23] as implemented in the VASP code [24, 25]. In particular, in our study we employed the PBE [26] flavor of GGA. The plane-wave basis set consists of all plane waves up to a kinetic energy of 450 eV. The molecule-Cu(110) system is modeled within the supercell approach and contains

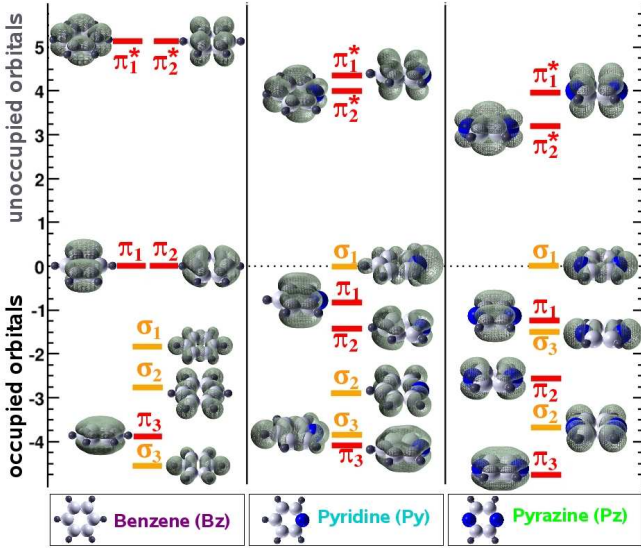


FIG. 1: (Color online) Energetic levels diagram for Bz (left), Py (middle) and Pz (right) molecules. Due to the presence of N atoms in the Py and Pz molecules the π -orbitals are shifted to lower energies while some of σ -orbitals are pushed to higher energies [34].

five atomic layers of copper with the adsorbed molecule on one side of the slab [27]. It was generated with the theoretical bulk copper lattice parameter of 3.63 \AA and has a $p(4 \times 6)$ in-plane surface unit cell. During our *ab initio* calculations, the uppermost two copper layers and the molecule atoms were allowed to relax until the atomic forces are lower than 0.001 eV/\AA .

The evaluation of the vdW forces by using the DFT-D [21, 22] method in the self-consistent cycle of our *ab initio* calculations are mandatory to obtain the proper equilibrium adsorption geometry and the corresponding electronic structure of the Py- and Pz-Cu(110) systems. Moreover, we also evaluated the correlation effects by using the vdW-DF functional [18] as a post processing procedure (i.e., non-self-consistent) on a charge density obtained from the standard GGA calculations [28] using the [29] code developed in our group.

As compared with Bz (C_6H_6), in the Py ($\text{C}_5\text{H}_5\text{N}$) molecule a CH group of atoms is replaced by a N atom, while the Pz ($\text{C}_4\text{H}_4\text{N}_2$) has two CH groups replaced by two N atoms. All molecules contain a 6π -electron system and they can adsorb with the molecular plane parallel to the Cu(110) surface [30, 31, 32]. From electronic point of view, it is well known [33, 34] that the presence of N atoms in the conjugated heterocycle molecules lower their π -orbitals while some of σ orbitals are pushed to higher energies. This peculiar feature is clearly shown in the energy levels diagram of the isolated Bz, Py, Pz molecules (see Fig. 1).

The Bz is considered to be chemisorbed on the Cu(110) surface [30, 31] due to an effective hybridization of the

p_z -atomic orbitals (those perpendicular to the molecular plane) with the Cu d -bands. Note that these p_z -atomic orbitals are forming the π -orbitals of the isolated molecule. On the contrary, in the case of Py and Pz molecules the presence of N atoms lower their π -orbitals which implies that the interaction of the corresponding p_z -atomic orbitals with the Cu d -bands is expected to be much weaker [33]. Indeed, using only the standard GGA approximations (PBE) in our DFT calculations of the flat adsorption geometry of Py and Pz molecules on Cu(110), we find that the adsorption site is not sensitive to the underlying geometry of the surface. The average Py(Pz)-surface metal distance is $2.98(2.99) \text{ \AA}$, while for the Bz this distance is 2.43 \AA . The magnitude of Py- and Pz-surface separation distances suggest that these molecules are physisorbed on Cu(110), while as already mentioned, the Bz is chemisorbed.

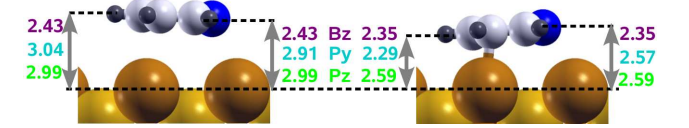


FIG. 2: (Color online) Side views of the relaxed geometries when using standard DFT (left panel) and DFT+D (right panel). The inclusion of the van der Waals interactions at a semi-empirical level in the DFT+D approach [22] decreases significantly the molecule-surface separation distance in the case of the Py and Pz molecules. The adsorbate-substrate distances are given in \AA .

In the next step we performed geometrical relaxations of the molecule-metal systems including the van der Waals forces using the DFT-D approach. Since the vdW forces are attractive, their effect is to bring the molecule closer to the surface (see Fig. 2). For the Bz molecule this effect on the adsorption geometry is not significant, since the average Bz-surface distance is decreased from 2.43 to 2.35 \AA . On the contrary, the inclusion of the long range dispersion effects has a huge impact on the geometry of the Py and Pz molecules adsorbed on Cu(110) surface. The average Py(Pz)-surface distance decreases significantly from $2.98(2.99)$ to $2.43(2.59) \text{ \AA}$. Also the tilt angle of the Py molecular plane changes from $+3^\circ$ (DFT) to $\approx -7^\circ$ (DFT+D).

This structural change drastically affects the *electronic structure* of the Py- and Pz-Cu(110) systems. In Fig. 3 we present the local density of states (LDOS) for Bz, Py and Pz molecules in the case of the relaxed geometries before (DFT) and after inclusion of the van der Waals forces (DFT+vdW). At the molecular site the basic characteristic displayed by the Bz-Cu(110) system are the broad bands with $\pi_{1,2,3}$ -character, while the σ ones are quite sharp and very localized on the molecule. Also this electronic structure is not affected by the inclusion of the long-range dispersion effects because the geometry of the system changes only slightly. On the contrary, for the Py and Pz molecules, due to a large molecule-metal

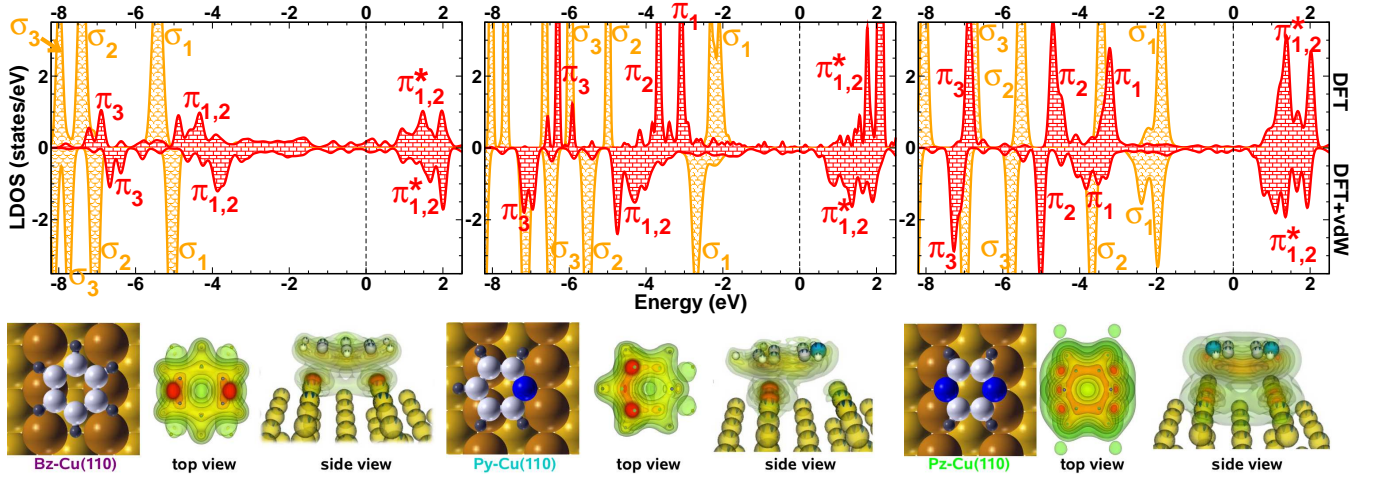


FIG. 3: (Color online) Upper panel: Local density of states (LDOS) of the Bz, Py and Pz molecules adsorbed on Cu(110). In the case of Bz molecule, the electronic structure of the molecule–surface system is not significantly modified by the inclusion of the dispersion effects. This is not the case of the Py– and Pz–Cu(110) systems, where the van der Waals attractive interaction brings the molecule closer to the surface and allows a stronger hybridization between the p_z –orbitals and the Cu d –bands. Lower panel: Binding energies due to nonlocal correlation effects evaluated with the vdW-DF method. Red color indicates a strong non-local (NL) contribution to the binding energy while green denotes a much weaker contribution. In the case of the Pz molecule this contribution is delocalized over the whole heterocycle ring while in the case of the Bz and Py it mainly arises from the two carbon sites that directly bind to the surface.

distance in the DFT relaxed geometry, the π bands are less broad being localized mainly on the molecules (see Fig. 3). The inclusion of the attractive van der Waals interaction brings the Py or Pz closer to the surface and thus it allows the p_z –orbitals to hybridize more strongly with the Cu d –bands. This molecule–surface interaction results in broad bands with mixed π and metallic character as already seen for the Bz–Cu(110) system. Note also the appearance in the case of Pz of a broad σ_1 type band.

To quantify the importance of the van der Waals interactions in the case of the flat adsorption process of the Bz, Py and Pz molecules on the Cu(110) surface, in Table I we report the calculated interaction E_{int} and adsorption E_{ads} energies defined as:

$$E_{\text{int/ads}} = E_{\text{sys}} - (E_{\text{molecule}}^{\text{relaxed/ideal}} + E_{\text{Cu(110)}}^{\text{relaxed/clean}}).$$

where E_{sys} represents the total energy of the relaxed molecule–Cu(110) system, $E_{\text{molecule}}^{\text{relaxed}}$ represents the total energy of the isolated molecule and $E_{\text{Cu(110)}}^{\text{relaxed}}$ is the energy of the Cu(110) surface, both the molecule and surface being in the same atomic configurations as in the relaxed molecule–Cu(110) system. Also, the $E_{\text{molecule}}^{\text{ideal}}$ denotes the total energy of the equilibrium isolated molecule and $E_{\text{Cu(110)}}^{\text{clean}}$ is the energy of the clean Cu(110) surface.

The interaction energy $E_{\text{int}}^{\text{DFT}}$ represents a measure of the strength of the chemical interaction between molecule and surface, while the adsorption one $E_{\text{ads}}^{\text{DFT}}$ includes not only the energy gain due to the bond formation ($E_{\text{int}}^{\text{DFT}}$) but also the energy paid to deform the molecules and

surface from their ideal configurations to those as found in the relaxed molecule–surface system.

	DFT relaxed		DFT+vdW relaxed			
	$E_{\text{int}}^{\text{DFT}}$	$E_{\text{ads}}^{\text{DFT}}$	$E_{\text{int}}^{\text{DFT}}$	$E_{\text{ads}}^{\text{DFT}}$	$E_{\text{ads}}^{\text{vdW-D}}$	$E_{\text{ads}}^{\text{vdW-DF}}$
Bz	-301	-253	-343	-252	-492	-543
Py	-115	-108	-196	-105	-417	-510
Pz	-35	-36	+56	+70	-371	-577

TABLE I: The interaction and adsorption energies of the Bz, Py and Pz molecules adsorbed on the Cu(110) surface (units: meV) for the geometries obtained using only DFT (left side) and DFT including the dispersion corrections (DFT+vdW, right side). Note that when the dispersion effects were considered, the adsorption and interaction energies have been decomposed into the contribution arising from a DFT ($E_{\text{ads,int}}^{\text{DFT}}$) and that given by the van der Waals corrections ($E_{\text{ads,int}}^{\text{vdW-D(F)}}$), i.e., $E_{\text{ads,int}}^{\text{DFT+vdW}} = E_{\text{ads,int}}^{\text{DFT}} + E_{\text{ads,int}}^{\text{vdW-D(F)}}$.

Although the molecular geometries are slightly distorted from a planar geometry after including the dispersion effects as compared to the those obtained only with DFT, for Bz and Py the calculated adsorption energies $E_{\text{ads}}^{\text{DFT}}$ are *practically invariant*. Moreover, the interaction energies $E_{\text{int}}^{\text{DFT}}$ are lower for the DFT+vdW relaxed geometries as compared to those calculated for the DFT relaxed ones. This theoretical finding implies that by including the van der Waals dispersions, the *chemical interaction* between the molecule and surface *increases*! This effect is rather small for Bz since this molecule is already chemically adsorbed on Cu(110) surface. However, the inclusion of the vdW interactions lowers significantly the interaction energy $E_{\text{int}}^{\text{DFT}}$ for Py on Cu(110). Also the average Py– and Bz–surface distances are now comparable (≈ 2.43 and 2.35 Å, respectively, see also Fig. 2).

In consequence, the Py molecule *becomes chemisorbed* on the Cu(110) surface. In this case, the the vdW attractive forces are the key ingredient that simply triggers the chemisorption process of Py on this surface. As regarding the Pz molecule, the $E_{\text{int}}^{\text{DFT}}$ indicates a weak bonding interaction (negative values) for the DFT relaxed geometries which turns into a repulsive interaction (positive values) after taking into account the dispersion effects. However, the adsorption energy due to the van der Waals interaction ($E_{\text{ads}}^{\text{vdW}}$) is much more negative as compared to $E_{\text{int}}^{\text{DFT}}$ such that the total value of the adsorption energy is negative. This means that the Pz molecule binds to the surface only through the van der Waals interaction.

In order to deeply understand how the correlation effects contribute to the molecule–metal interaction, in Fig. 3 we plotted the binding energies due to the non-local (NL) correlation effects as calculated within the vdW-DF theory [18]. For the Bz and Py molecules, the non-local contribution is mainly localized in the regions where the C atoms are situated on top of Cu atoms of the surface. In the case of Pz, the contribution of the non-local correlation effects is much more delocalized over the entire molecule. From the electronic structure point of view, this peculiar feature is related to a larger contribution to the NL part of the binding energy of the σ_1 molecular orbital in the case of the Pz with respect to the Py molecule. Note that for Bz this contribution is not significant since the σ_1 lies deep in energy with respect to the Fermi energy of the molecule-surface system. Therefore which molecular orbitals will contribute to the vdW interactions clearly depends on the specific alignment of these orbitals at the molecule-surface interface. An animation is available as additional material[35].

To conclude, we prove that the van der Waals dispersion effects together with the corresponding vdW attractive forces are crucial to reliably calculate in a self-consistent manner the proper equilibrium adsorption geometry and the corresponding electronic structure of π -conjugated heterocycle molecules adsorbed on Cu(110) surface. The inclusion of the long-range dispersion effects changes *qualitatively* the adsorption process of Py ($\text{C}_5\text{H}_5\text{N}$) on Cu(110) surface from *physisorption* to *chemisorption*, while for the Pz ($\text{C}_4\text{H}_4\text{N}_2$) the van der Waals interactions represent the driving forces which bind the molecule to the surface. Our study also clearly pointed out that the vdW interactions depends on the alignment of the molecular orbitals at adsorbate-substrate interface and can involve not only π -like orbitals (perpendicular to the molecular plane) but also σ -like orbitals (in the molecular plane). Therefore we conclude that these effects will definitely play a key role in the adsorption process of other π -conjugated heterocycle molecules as porphyrines or phthalocyanine on metal surfaces.

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